bondlines form when the reaction mixture divides into multiple flow fronts as it flows around the part and the separate flow fronts meet. When the polyurethane does not adhere to itself very strongly, cracks appear at the bondlines. This leads to a loss of thermal insulation efficiency and can expose the underlying substrate to the corrosive effects of seawater.

What is needed in the art is a method of making a syntactic polyurethane elastomer, which does not contain a mercury catalyst, which is resistant to cracking even when cast in confined complex geometries and which bonds well to itself.

This disclosure is in one embodiment a cured syntactic polyurethane elastomer which is a reaction product of a reaction mixture comprising an alkylene glycol chain extender, 5 to 50 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, and (iii) the reaction mixture is essentially devoid of mercury compounds.

The disclosure is also a method for making a syntactic polyurethane elastomer, comprising

a) forming a reaction mixture containing an alkylene glycol chain extender, 5 to 50 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, and (iii) the reaction mixture is essentially devoid of mercury compounds, and

b) curing the reaction mixture to form the syntactic polyurethane elastomer.

Surprisingly, the syntactic polyurethane elastomer of the disclosure is morphologically very similar to conventional syntactic polyurethane elastomers made in a one-step process (*i.e.*, without first forming a prepolymer by reacting

reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, and (iii) the reaction mixture is essentially devoid of mercury compounds, to at least a portion of the substrate and (2) at least partially curing the first reaction mixture to form the first section of syntactic polyurethane elastomer, and then

b) forming a second section of syntactic polyurethane elastomer on at least a portion of the substrate by (1) applying a second reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, and (iii) the reaction mixture is essentially devoid of mercury compounds to at least a portion of the substrate and in contact with the first section of syntactic polyurethane elastomer to form at least one bondline between the first section of syntactic polyurethane elastomer and the second reaction mixture and (2) at least partially curing the second reaction mixture to form the second section of syntactic polyurethane elastomer adherent to the first section of syntactic polyurethane elastomer.

In one aspect, there is provided a process for producing a substrate having an applied syntactic polyurethane elastomer, comprising

a) forming a section of a syntactic polyurethane elastomer on at least a portion of the substrate by (1) applying a first reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is

sufficient to provide an isocyanate index of 80 to 130, (iii) wherein the non-mercury catalyst is a zinc carboxylate or a mixture of 98-99.99 weight percent of one or more zinc carboxylates and 0.01 to 2 weight percent of one or more zirconium carboxylates and (iv) the reaction mixture is essentially devoid of mercury compounds, to at least a portion of the substrate and (2) curing the first reaction mixture until it has developed enough green strength to maintain its shape, to form the first section of syntactic polyurethane elastomer, and then

b) forming a second section of syntactic polyurethane elastomer on at least a portion of the substrate by (1) applying a second reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, (iii) wherein the non-mercury catalyst is a zinc carboxylate or a mixture of 98-99.99 weight percent of one or more zinc carboxylates and 0.01 to 2 weight percent of one or more zirconium carboxylates and (iv) the reaction mixture is essentially devoid of mercury compounds to at least a portion of the substrate and in contact with the first section of syntactic polyurethane elastomer to form at least one bondline between the first section of syntactic polyurethane elastomer and the second reaction mixture and (2) at least partially curing the second reaction mixture to form the second section of syntactic polyurethane elastomer adherent to the first section of syntactic polyurethane elastomer.

Figure 1 is dynamic mechanical analysis curve for an embodiment of the invention.

Figure 2a) is a micrograph of a syntactic polyurethane elastomer of the invention.

Figure 2b) is a micrograph of a prior art syntactic polyurethane elastomer.

Figure 2c) is a micrograph of a prior art syntactic polyurethane elastomer.

For purposes of this invention, a chain extender is one or more compounds having two to three hydroxyl groups and a hydroxyl equivalent weight of up to 125. A preferred type of chain extender is an aliphatic glycol or glycol ether. The aliphatic glycol is a straight-chain or branched alkane having two hydroxyl

WHAT IS CLAIMED IS:

1. A process for producing a substrate having an applied syntactic polyurethane elastomer, comprising

a) forming a section of a syntactic polyurethane elastomer on at least a portion of the substrate by (1) applying a first reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, (iii) wherein the non-mercury catalyst is a zinc carboxylate or a mixture of 98-99.99 weight percent of one or more zinc carboxylates and 0.01 to 2 weight percent of one or more zirconium carboxylates and (iv) the reaction mixture is essentially devoid of mercury compounds, to at least a portion of the substrate and (2) curing the first reaction mixture until it has developed enough green strength to maintain its shape, to form the first section of syntactic polyurethane elastomer, and then

b) forming a second section of syntactic polyurethane elastomer on at least a portion of the substrate by (1) applying a second reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, (iii) wherein the non-mercury catalyst is a zinc carboxylate or a mixture of 98-99.99 weight percent of one or more zinc carboxylates and 0.01 to 2 weight percent of one or more zirconium carboxylates and (iv) the reaction mixture is essentially devoid of mercury compounds to at least a portion of the substrate and in contact with the first section of syntactic polyurethane elastomer to form at least one bondline between the first section of syntactic polyurethane elastomer and the second reaction mixture and (2) at least partially curing the second reaction mixture to form the second section of syntactic polyurethane elastomer adherent to the first section of syntactic polyurethane elastomer.

2. The process of claim 1 wherein the bondline has a bond strength of at least 8.0 MPa as measured according to ASTM D638.

3. The process of claim 1 wherein the substrate is an undersea pipe or undersea architecture.

4. The process of claim 3 wherein the undersea pipe or undersea architecture is branched, curved or has another non-linear configuration.

5. The process of claim 4 wherein the undersea pipe or undersea architecture has one or more external features that protrude partially or completely through the applied syntactic polyurethane elastomer.

6. The process of claim 1, wherein the polyether polyol used to make the isocyanate-terminated prepolymer is prepared by (A) adding propylene oxide and ethylene oxide to a difunctional or trifunctional initiator to produce a polyol having a hydroxyl equivalent weight of 1500 to 2500 and containing 5 to 30% by weight polymerized ethylene oxide, wherein the polymerized ethylene oxide is randomly polymerized with the propylene oxide, forms one or more internal blocks and/or forms terminal blocks that result in primary hydroxyl groups or (B). homopolymerizing propylene oxide or randomly copolymerizing 75-99.9 weight percent propylene oxide and 0.1 to 25 weight percent ethylene oxide onto a trifunctional initiator, and optionally capping the resulting polyether with up to 30% by weight (based on total product weight) ethylene oxide to form a polyether polyol having an equivalent weight of 1500 to 2500.

7. The process of claim 6, wherein the chain extender is 1,4-butanediol.

8. The process of claim 1 wherein each respective reaction mixture contains 15 to 25 weight percent microspheres.